

UNITED STATES PATENT OFFICE

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PROCESS FOR THE PREPARATION OF
FILMS AND FILAMENTS AND PROD-
UCTS THEREOF

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This invention relates to the preparation of films and filaments and similar unsupported structures and more particularly to the prepara-
5 tion of such structures from at least partially deacetylated but substantially undegraded chitin.

Chitin is a polymeric acetamino carbohydrate derivative occurring in the shells of various crustacea such as shrimps, crabs, lobsters, and the like, as well as in the horny exo-skeleton of various insects such as beetles, locusts, grasshoppers, and the like. Chitin has a structure related to that of cellulose, the glucose structural unit of the cellulose being replaced by an acetylated hexose-amine. On hydrolysis under regulated conditions, an at least partially deacetylated
10 chitin may be prepared from purified chitin without substantial degradation. A completely deacetylated material has been obtained by drastic hydrolysis but this material has undergone substantial degradation. The subject is reviewed by
15 Wester in Archiv der Pharmazie 247 282-307 (1909).

This invention has as an object the preparation of technically useful articles such as unsupported
20 films and filaments from at least partially deacetylated substantially undegraded chitin. A further object is the further improvement of these films and filaments. Other objects will appear hereinafter.

These objects are accomplished by the following invention wherein a mass, swollen by but preferably in solution in dilute acid, of an at least partially deacetylated but substantially undegraded chitin, is coagulated in the form of a
25 shaped object preferably having at least one dimension relatively large and one dimension relatively small, i. e., in the form of a film, thread, or a filament.

In the process of the present invention, solutions of at least partially deacetylated but substantially undegraded chitin are preferably used. The preparation of suitable solutions is shown in copending application Serial No. 731,600 filed June 21, 1934. In general, it may be stated that
30 a partially deacetylated chitin of suitable properties may be obtained by regulated hydrolysis of a purified chitin. The method of purification disclosed in the above application consists first, in boiling the chitin-containing material with a 1% sodium carbonate solution for six hours, filtering, then treating with 5% hydrochloric acid solution to remove lime salts, filtering and again boiling with a 1% sodium carbonate solution, this time with the addition of a detergent material
35 such as soap. The purified chitin thus obtained

is at least partially deacetylated by heating with caustic solutions at elevated temperatures. The caustic may range in concentration from 5% to 60% by weight and the temperature as high even as 150° C., the higher concentrations of caustic requiring a lower temperature and/or a shorter time of deacetylation, thus approximately the same results are obtained with 5% caustic at 150° C. for twenty-four hours, 50% caustic at 100° C. for one hour, and 40% caustic at 100° C. for eighteen hours. The hydrolysis step is continued until a product at least swollen by but preferably soluble in dilute acetic acid is obtained, but is discontinued before the product becomes degraded. Products in which from .2 to .9 or even more of the acetyl groups have been removed by hydrolysis thus leaving from .2 to .9 or even more of the nitrogen as free amino are suitable, but for many purposes a product containing about 70% to 86% of the nitrogen in the form of the free amino group is preferred. The product containing only about .2 of its total nitrogen as free amino nitrogen is swollen, but not completely dissolved by dilute acetic acid. The viscosity of the final product may be controlled by the use of the different temperatures of deacetylation, different concentrations of caustic, different lengths of caustic treatment and by controlled oxidation, as for example, by the addition of small quantities of hydrogen peroxide or by bubbling air through solutions of deacetylated chitin. These treatments reduce the solution viscosity of the deacetylated chitin. The solution viscosity may also be increased by heating the dry deacetylated chitin as disclosed in the above application.

The solution of deacetylated chitin obtained by dissolving deacetylated chitin prepared as shown above in dilute acetic or other acids, may be cast, spun, extruded, etc., into various shapes in order to obtain the articles of the present invention.

Since deacetylated chitin is essentially a highly polymeric free primary amine it forms salts with acids. Many of these salts are water soluble. The following table lists some of the acids whose salts of deacetylated chitin have been prepared. These salts are prepared from substantially undegraded, partially deacetylated chitin containing about .8 free amino groups per chitosamine residue. The salts however may be prepared with other ranges of free amino content. Thus, deacetylated chitins with 70% to 86% of their nitrogen in the form of free amino groups are preferred altho products containing as low as 20% of the nitrogen in the form of free amino